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The kinetics and mechanisms of the reaction of benzyl chloride with potassium t-butoxide in t-butyl alcohol

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Department:

THE KINETICS AND MECHANISMS OF THE REACTION OF BENZYL CHLORIDE WITH POTASSIUM t-BUTOXIDE IN t-BUTYL ALCOHOL

BY

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A

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I. INTRODUCTION

Benzyl chloride is a moderately reactive halide. Substitution of the Cl^- by other nucleophiles, e.g., HO^-, AcO^-, $S_2O_3^-$, Br^- etc. proceeds almost quantitatively in solutions at convenient temperatures.

$$C_6H_5CH_2Cl + Y^- \longrightarrow C_6H_5CH_2Y + Cl^-$$

However, with the very strong nucleophilic base NH_2^- in liquid ammonia, benzyl halides undergo an eliminative condensation reaction leading to the formation of stilbene.

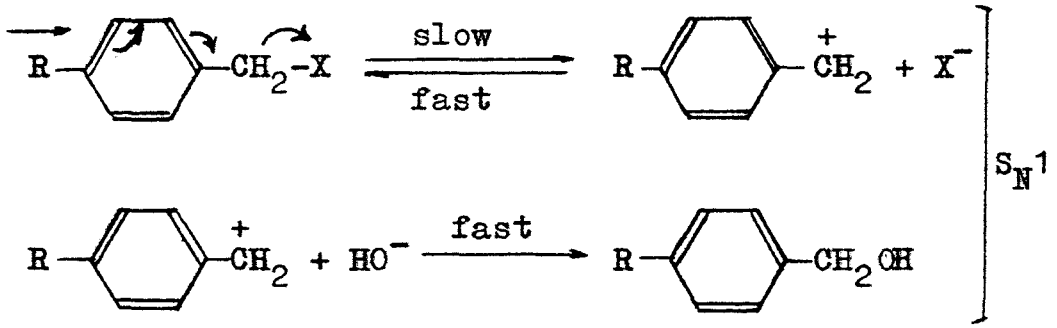
$$2C_6H_5CH_2Cl \xrightarrow[\text{Liq. } NH_3]{NaNH_2} C_6H_5CH{=}CHC_6H_5$$

The object of this study was to investigate if the less basic t-butoxide in t-butyl alcohol would afford the same product, viz., stilbene; and, if so, by what mechanism. A study of the products and kinetics of the interaction between benzyl chloride and potassium t-butoxide in t-butyl alcohol therefore has been initiated.

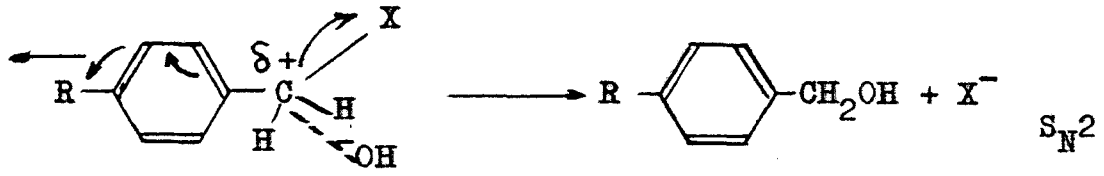
The pertinent literautre is reviewed in Chapter II. Chapter III deals with the experimental work, while Chapter IV presents the results and deals with an attempt to formulate a mechanism for the reaction studied.

II. REVIEW OF LITERATURE

The alkaline hydrolysis of substituted benzyl chlorides in aqueous-aprotic solvent mixtures can be approximated as the sum of two reactions: one independent of the reagent hydroxide ion, i.e., S_N1, and the other proportional to its concentration, i.e., S_N2.[1,2]



(The ionization of (X) is retarded by electron-attracting groups.)



(The approach of the HO^- is facilitated by electron-attracting groups.)

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(1) S. C. J. Olivier, Rec. trav. chim., 49, 687 & 996 (1930).

(2) M. Simonatta & G. Favini, J. Chem. Soc., 1840-4 (1954).

The two aralkyl series:

$R = CH_3$ CH_2Ph $CHPh_2$ CPh_3

and $R =$ CH_2Ph $CHMePh$ CMe_2Ph

have been studied sufficiently to locate the change of mechanism, the first series with respect to both the aqueous reactions

$$HO^- + R\text{-}Hal \longrightarrow R\text{-}OH + Hal^-$$

$$HO^- + (R\text{-}NR_3)^+ \longrightarrow R\text{-}OH + NR_3$$

and the second with respect only to the halide substitution; and it was concluded that benzyl chloride itself belongs to the mechanistic boarder region. Members to the right in either series undergo unimolecular reactions. "The molecular reason", says Ingold,[3] "why we should not expect the change from a bimolecular to a unimolecular mechanism to be sharp follows from an elementary picture of the two processes. In one, the expelled group is liberated with help from the attacking reagent; in the other, the liberated group gets free without such help; and yet, there must be degrees of assistance which could be offered by the substituting agent and accepted by the heterolyzing system.[4]"

Even, within the substituted benzyl chlorides a wide variation in the extent of operation of S_N1 and S_N2 mechanism is expected. A strong electron-attracting group

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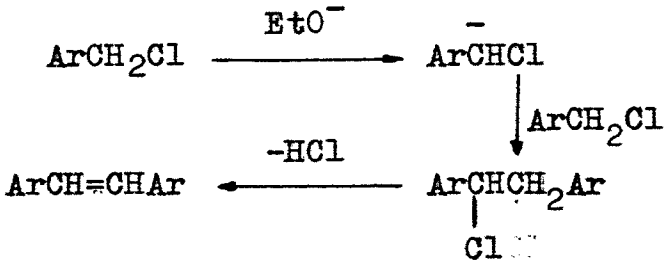
(3) C. K. Ingold, "Structure and Mechanism in Organic Chemistry", Cornell University Press, Ithaca, 1953, p 324.

(4) J.LGleave,E.D.Hughes & C.K.Ingold,J.Chem.Soc.,235(1935).

would increase the S_N2 character on the expense of S_N1, and vice-a-versa for strong electron-repelling groups.[2]

It should be pointed out, however, that o- and p-nitrobenzyl chlorides are converted by alcoholic potassium hydroxide to a mixture of cis- and trans-nitrostilbenes.[5] Bergmann and Hervey[6] suggested that the reaction of o- or p-nitrobenzyl halides with sodium ethoxide to give a dinitrostilbene is initiated by an α-dehydrohalogenation. Kleucker,[7] however, pointed out that the reaction may involve consecutive carbanion formation, alkylation, and dehydrohalogenation.



Similarly for the formation of p,p'-dinitrostilbene oxide from p-nitrobenzaldehyde and p-nitrobenzyl chloride in the presence of base either a methylene mechanism or a condensation-dehydrohalogenation mechanism may be written.

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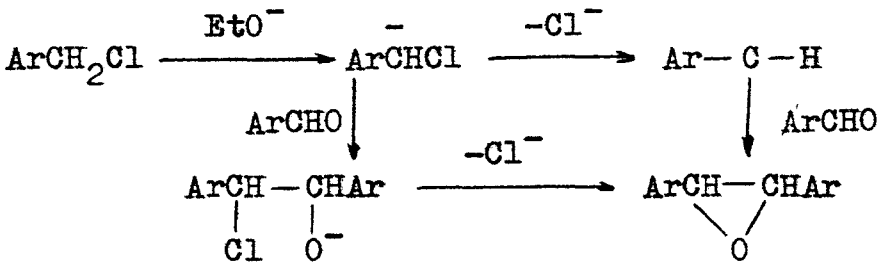
(5) P. Walden & A. Kernbaum, Chem. Ber., 23, 1959 (1890).

(6) E. Bergmann & J. Hervey, Chem. Ber., 62, 893 (1929).

(7) E. Kleucker, Chem. Ber., 62, 2587 (1929).



Hanna, Iskander, and Riad[8] carried out a kinetic investigation to determine whether or not these reactions of p-nitrobenzyl halides with base involve the formation of p-nitrophenylmethylene. The reaction of p-nitrobenzyl chloride with sodium hydroxide in aqueous dioxane and in aqueous acetone (to give p,p'-dinitrostilbene "almost quantitatively") was reported to be first-order in base and first-order in halide. Assuming that no more than a very small fraction of the material is ever present in the form of the various intermediates at any given time, this is the kinetic order that would be expected for the methylene mechanism if either the formation of the carbanion or its decomposition to methylene is rate-controlling. The alkylation-dehydrohalogenation mechanism for the formation of dinitrostilbene would also lead to these kinetics if carbanion formation were the rate-controlling step of the reaction. This cannot be the case, however, because the unreacted p-nitrobenzyl chloride recovered from treatment with base in dioxane-deuterium

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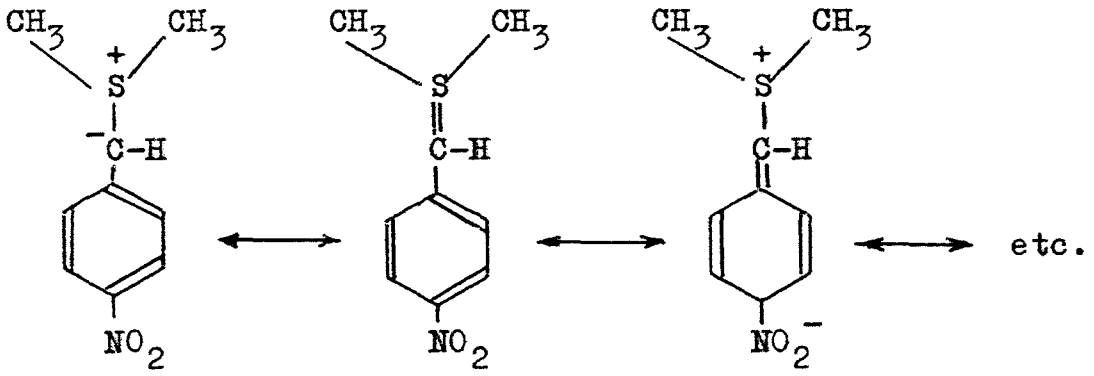
(8) S. B. Hanna, Y. Iskander, & Y. Riad, J. Chem. Soc., 217 (1961).

oxide contained about 0.42 deuterium atom per molecule after a time during which about 38 per cent of the halide should have been transformed to dinitrostilbene. This shows that the first step of the reaction is reversible, with the carbanion being protonated at a rate comparable to its rate of further reaction. In this case the reaction rate by the alkylation-dehydrohalogenation mechanism should show a greater-than-first-order dependence on the concentration of p-nitrobenzyl chloride, and thus this mechanism may be ruled out on the basis of Hanna, Iskander, and Riad's evidence.

By contrast, the rate of formation of p,p'-dinitrostilbene oxide from p-nitrobenzaldehyde, p-nitrobenzyl chloride, and base was found to increase with increasing aldehyde concentration, showing that the rate-controlling step of the reaction is not methylene formation but probably combination of the aldehyde with a carbanion derived from p-nitrobenzyl chloride.

Although the report by Hanna, Iskander, and Riad is in agreement with the hypothesis that a methylene intermediate is formed in the reaction, it gives no direct evidence concerning the mechanism by which the methylene is transformed to p,p'-dinitrostilbene. This point will be discussed in relation to a closely related study of the reaction of p-nitrobenzyldimethylsulfonium ions with sodium hydroxide that was carried out by Swain and Thornton.

These workers studied the reaction in dilute aqueous solution (where the total yield of cis- and trans-p,p'-dinitrostilbene is 99 per cent) in the presence of 0.3 M sodium perchlorate to minimize the effect of changing ionic strength.[9] The organic reactant was found to undergo base-catalyzed deuterium exchange much more rapidly than it formed dinitrostilbene, showing that carbanion formation cannot be rate-controlling. The basic reaction mixture was slightly orange, presumably because of the presence of small amounts of the carbanion.



When a pellet of potassium hydroxide was added to the solution a deep crimson color surrounded it as it dissolved. This observation prompted Swain and Thornton, despite its lacking spectrophotometric confirmation, to assume that the light orange color stemmed from the conversion of only a small fraction of the sulphonium salt to its carbanion. Since it therefore appears that the steady state assumption can be made for the carbanion, the observation that the reaction is first-order in base and first-order in sulfonium salt rules out

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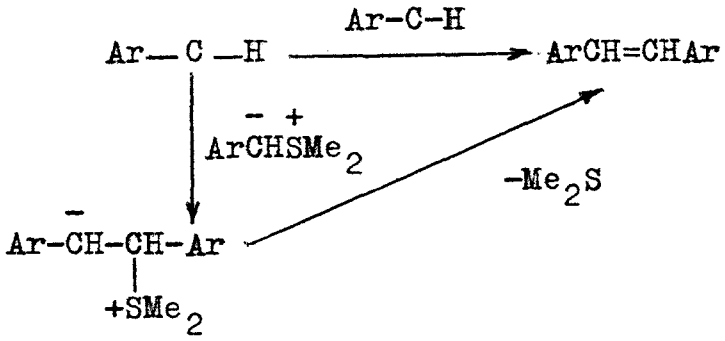
(9) C. G. Swain & E. R. Thornton, J. Am. Chem. Soc., 83, 4033 (1961).

an alkylation-elimination mechanism for the reaction, but is in agreement with a mechanism involving rate-controlling loss of dimethyl sulfide from the intermediate carbanion to give p-nitrophenylmethylene. This methylene may either dimerize or add to a carbanion and then undergo an elimination reaction.



On the basis of the sulfur kinetic isotope effect, which is less than half as large as that observed in the solvolysis of t-butyldimethylsulfonium ions, Swain and Thornton argue that the methylene does not dimerize but adds to carbanions. It is not clear, however, that the kinetic isotope effect in the present case can be predicted with the reliability required by this agrument. In either case the 99 per cent yield of dinitrostilbene obtained from 0.1 M sulfonium salt and 0.2 M sodium hydroxide in aqueous solution (55 M water) shows that if a methylene is indeed formed in the reaction it is a very highly selective species since it appears to react with carbanions that are present at a concentration probably no larger than 0.01 M or with a methylene whose concentration is probably much smaller,

rather than with the much more abundant species hydroxide ion and water. In reaction with the intermediate methylene another methylene molecule has the advantage of leading directly to a stable molecule, but the carbanion probably has the advantage of being present at a higher concentration.

Bergstrom and Fernelius[10] reported that even benzyl chloride exhibits this type of reaction to form stilbene with potassium amide in liquid ammonia, while Kharasch and co-workers[11] obtained a quantitative yield of this dimeric olefin with sodium amide in this medium.

$$2C_6H_5CH_2Cl \xrightarrow[\text{Liq. } NH_3]{NaNH_2} C_6H_5CH{=}CHC_6H_5$$

The condensation of benzyl chloride by iron and water to give trans-stilbene has been reported.[12] Hoeg and Lusk[13] reported the formation of trans-stilbene from reaction of n-butyllithium with benzyl chloride in tetrahydrofuran. It is evident that there are a number of ways and mechanisms by which benzyl chloride is tranformed into stilbene. Closs and Closs found that the reaction of benzyl chloride with

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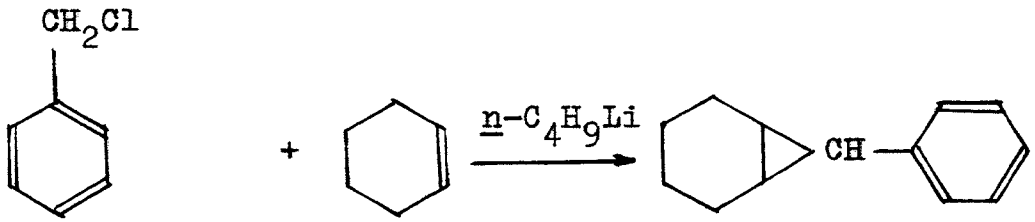
(10) F. W. Bergstrom & W. C. Fernelius, Chem. Rev., 20, 435 (1947).

(11) M. S. Kharasch, W. Nudenberg & E. K. Fields, J. Am. Chem. Soc., 66, 1276 (1944).

(12) Y. Ogata & H. Nakamura, J. Org. Chem. 21, 1170 (1956).

(13) D. F. Hoeg & D. I. Lust, J. Am. Chem. Soc., 86, 928 (1964).

n-butyllithium in ether and cyclohexene leads to the formation of 14 per cent 7-phenylbicyclo-[4.1.0] heptane, among other products.[14]



This observation may be explained on the basis of the initial α-dehydrochlorination of benzyl chloride to give phenylmethylene, which then adds to the olefinic double bond; but, in view of the fact that the formation of cyclopropane derivatives is not in itself adequate evidence for the intermediacy of methylenes and the fact that the reaction of benzyl chloride with sodamide may not give phenylmethylene, it is believed that the elucidation of the mechanism of the reaction of benzyl chloride with butyllithium requires further study. The same may be said of the reaction of benzyl phenyl ether with butyllithium, found by Schollkopf and Eisert[15] to yield a small amount of 1,1-dimethyl-2-phenylcyclopropane when carried out in the presence of isobutylene, or a little benzylidenetriphenylphosphine when carried out in the presence of triphenyl-

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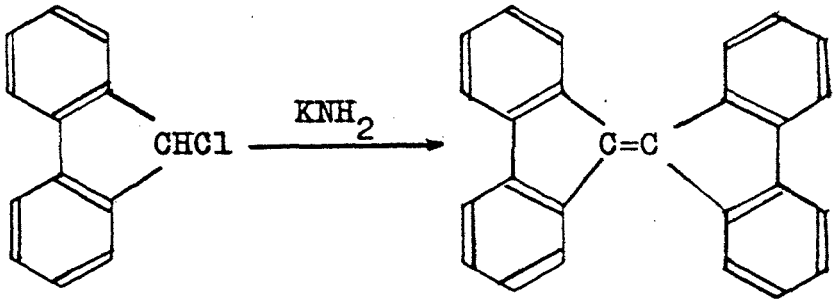
(14) G. L. Closs & L. E. Closs, Tetrahedron Letters, no.24, 26 (1960).

(15) U. Schollkopf & M. Eisert, Ann., 664, 76 (1963).

phosphine.

$$C_6H_5CH_2OC_6H_5 + \underline{n}\text{-BuLi} \xrightarrow{(C_6H_5)_3P} (C_6H_5)_3P{=}CHC_6H_5$$

$\Delta^{9,9'}$-bifluorene was obtained from 9-bromofluorene and potassium hydroxide in methanol-acetone by Thiele and Wanscheidt,[16] from 9-fluorenyltrimethylammonium hydroxide by Ingold and Jessop,[17] and from 9-chlorofluorene and potassium amide by Hauser and coworkers.[18]



Bethell's observations that the formation of $\Delta^{9,9'}$-bifluorene from 9-bromofluprene and potassium <u>t</u>-butoxide in <u>t</u>-butyl alcohol is first-order in base and second-order in organic halide, and that the base-catalyzed deuterium exchange of 9-deuterio-9-bromofluorene is rapid compared to the formation of bifluorene, show that the alkylation-

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(16) J. Thiele & A. Wanscheidt, Liebigs Ann. Chem. <u>376</u>, 278 (1910).

(17) J. A. Jessop & C. K. Ingold, J. Chem. Soc., 2357 (1929).

(18) C. R. Hauser, W. R. Brasen, P. S. Skell, S. W. Kantor, & A. E. Brodhag, J. Am. Chem. Soc., <u>78</u>, 1653 (1956).

elimination mechanism is very probably operative.[19]

Excellent reviews on the subject of α-elimination have appeared within the last two years.[20]

Since no rate-measurement have been done concerning the interaction of benzyl chloride with strong base, and since such measurements are necessary for formulating a mechanism, it appeared necessary to carry out such an investigation. The interaction of benzyl chloride with sodium amide in liquid ammonia would be an ideal system to study since the product, stilbene, is formed quantitatively.[11] However, in the face of technical difficulties (working with liquid ammonia) it was thought feasible to try the benzyl chloride - t-butoxide in t-butyl alcohol system.

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(19) D. Bethell, J. Chem. Soc., 666 (1963).

(20) W. Kirmse, Angew. Chem. (International Edition in English), 4, 1 (1965); J. Hine, "Divalent Carbon", Ronald Press, New York 1964; W. Kirmse, "Carbene Chemistry", Academic Press, New York 1964.

III. EXPERIMENTAL

The experimental part of this work will be treated under the following three sections:

A. Preparation of the materials to be studied.

B. Qualitative investigation of the products of the reactions.

C. Kinetic technique and rate measurements, comprising results and graphical representations.

A. PREPARATION OF MATERIALS

The following materials were either prepared or purchased and purified according to standard procedures.

Benzyl chloride, material of laboratory analytical reagent grade was distilled in vacuum using a short-path fractional distillation apparatus as shown in Fig. 1. The colourless product was kept away from light in a bottle covered with black paper.

t-Butyl alcohol was purified by distillation over sodium metal through the apparatus shown in Fig. 2. The middle fraction, boiling at 83°C. was collected with precautions to exclude moisture, and was kept in a pyrex glass-stoppered bottle.

Silver nitrate solution was prepared by weighing 2.0842 grams of silver nitrate and dissolving in distilled water to make 2 liters. The calculated molarity is 0.00614.

Potassium t-butoxide solution was obtained by dissolving freshly cut potassium metal in distilled t-butyl alcohol. Freshly prepared potassium t-butoxide solutions were used for all experiments.

Hydrochloric acid, standardized by titration against sodium carbonate using methyl orange as indicator, was used to determine the concentration of potassium t-butoxide.

Sodium chloride solution used for standardization of the silver nitrate solution was prepared by dissolving 0.3287 gram of pure sodium chloride in one liter solution. The molarity of this solution is 0.00562.

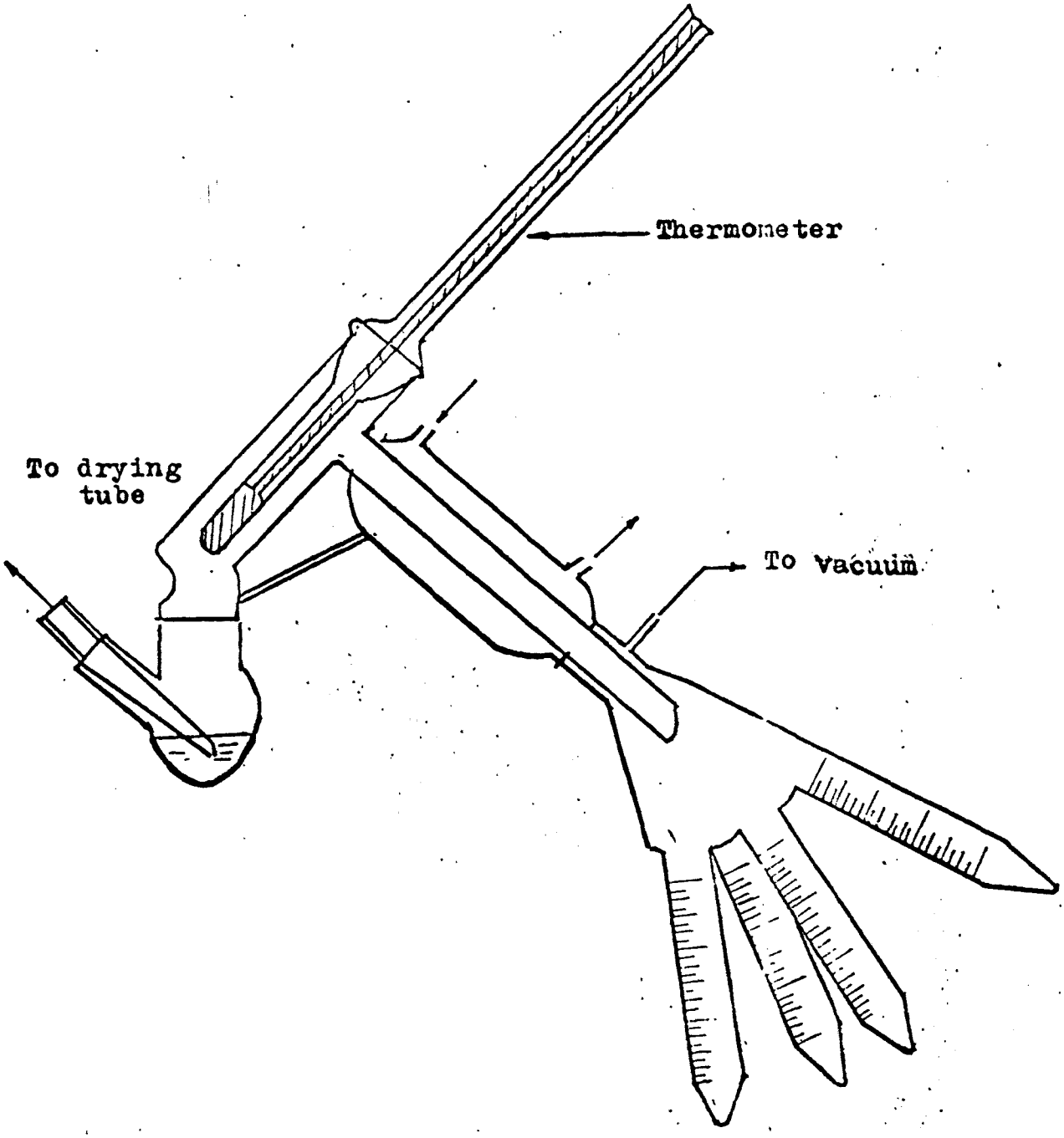

Fig. 1 SHORT-PATH FRACTIONAL DISTILLATION

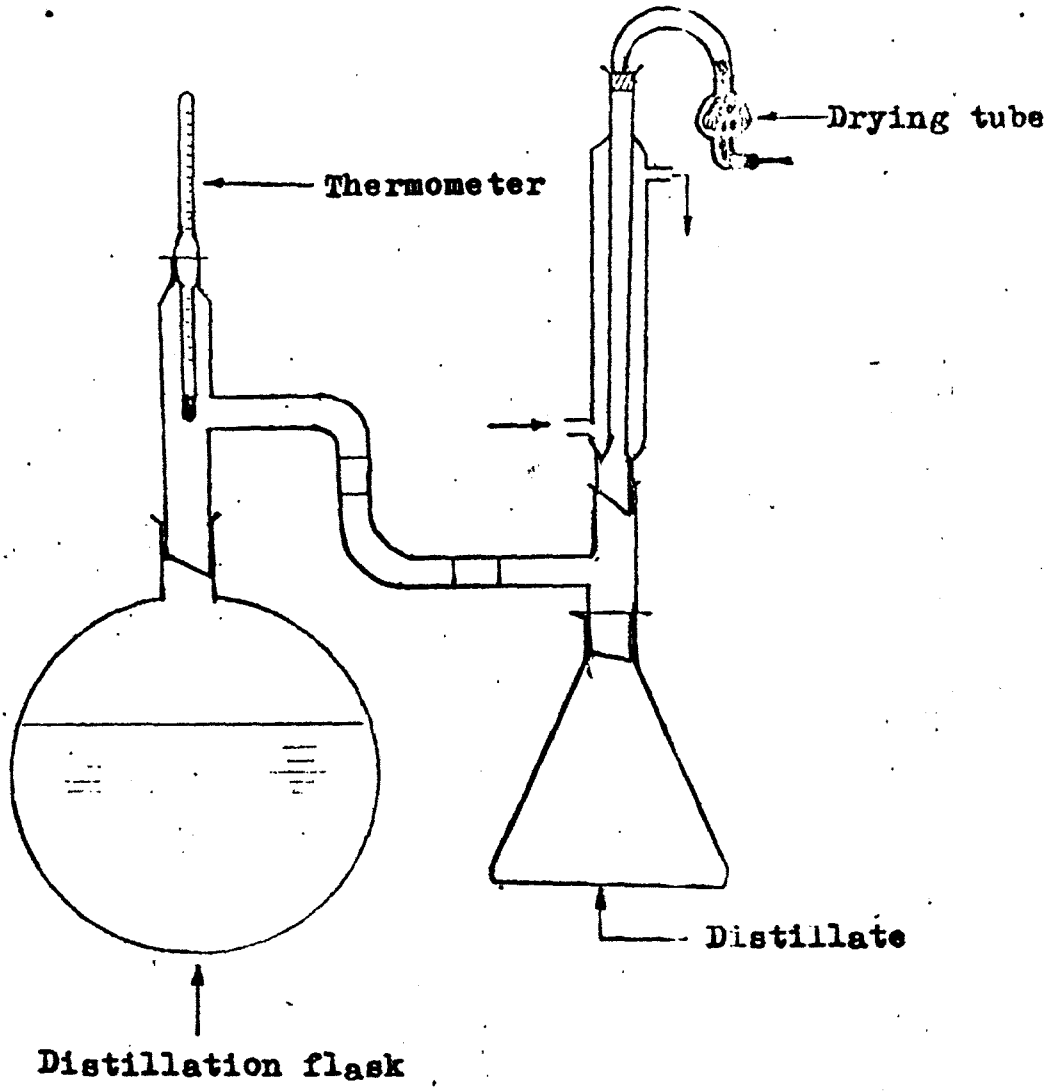

Fig. 2 DISTILLATION OF t-BUTYL ALCOHOL

B. QUALITATIVE INVESTIGATION OF THE PRODUCTS OF REACTION

Benzyl chloride was allowed to react with potassium t-butoxide in t-butyl alcohol, at refluxing temperature, for a period of time sufficient to insure complete transformation of the covalent chloride into ionic chloride. The initial concentration of benzyl chloride was 0.1 M, and that of potassium t-butoxide was about 0.2 M. The reaction mixture was neutralized with concentrated hydrochloric acid and the precipitated potassium chloride filtered off. The filtrate, after dilution with an equal volume of water, was extracted with ether several times, and the collected ether extracts subjected to gentle distillation to remove the ether. Most of the extracted t-butyl alcohol was removed on the rotary evaporator at a temperature of about 50°C. The remainder, a mixture of oil and shiny crystalline flakes, was identified as a mixture of cis- and trans-stilbenes by smell, by comparing its gas chromatograph with that of an authentic sample prepared by Mr. R. Steinkamp, and by formation of the dibromo derivative. The latter was prepared by adding bromine im ether to the reaction product in ether, and subjecting the reaction mixture to sun light. The once clear solution of reactants developed turbidity suddenly with separation of tiny white crystals of the dibromostilbene, m.p. 235°C; lit. 237°C.[18]

C. KINETIC TECHNIQUES AND RATE MEASUREMENTS

METHOD OF ANALYSIS: The kinetic investigations in the present work consisted essentially of determining the amount of chloride ion liberated at different intervals of time. An electrometric method for the determination of chloride ions was used.

In this simple and rapid method, due to R. J. Best,[20] a silver wire coated with silver chloride dips into the solution of unknown concentration, and is connected to a quinhydrone half-cell by means of an agar-potassium nitrate bridge. At the end point, in the titration of a chloride solution with silver nitrate, the chloride ion concentration is 1.0×10^{-5} (the solubility product of silver chloride = 1.0×10^{-10}) at 25°C., and the theoretical potential of a silver-silver chloride electrode in this solution would be -0.521 V. If, therefore, this electrode is connected with a quinhydrone reference half-cell giving a steady potential of +0.521 V., the combination will have zero potential at the end point of the titration. A quinhydrone half-cell made from a buffer solution of pH3.03 meets these requirements at a temperautre of 25°C. At 16°C., the calculated pH of the reference half-cell is 3.30. In practice, the buffer solution can have any value between 3.0 and 3.3

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(20) R. J. Best, J. Agric. Sci., 19, 533 (1929).

without introducing an error greater than one drop of 0.005 M silver nitrate in the usual volume titrated, for all temperatures between 16° and 25°C.

The end point is denoted by a reversal of the direction of current, for the Ag-AgCl electrode is negative with respect to the quinhydrone electrode as long as free chloride ions remain in solution. As the titration proceeds and silver nitrate is added, the potential difference decreases until, at the theoretical end point, it is zero. The further addition of silver nitrate solution causes the Ag-AgCl electrode to become the positive pole so that a reversal of current occurs at this point. With suitable galvanometer in circuit, this reversal of current can be easily detected to within one drop of 0.005 M silver nitrate.

The titrations were carried out in a medium of pH about 2, using sulphuric acid as the acidifying agent.[21]

Reagents:

a) Buffer solution of pH 3.2: 10.21 grams of potassium hydrogen phthalate were dissolved in distilled water, 148 ml. of 0.1 M sulfuric acid were added, the solution diluted to 1 liter, and stored in a stoppered pyrex bottle. The pH when checked with a pH meter was 3.25.

b) Quinhydrone reference half-cell: An analytical grade of quinhydrone and conventional electrode vessel were

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(21) A. H. Snyder, Soil Sci., 35, 43 (1933).

used. Before use, the platinum electrode was cleaned with a hot mixture of chromic and sulphuric acids, washed well with distilled water, and heated to redness in an alcohol flame for a few seconds to ensure constancy and correctness of potential. The electrode solution was prepared by dissolving a small amount of quinhydrone in the buffer solution in the half-cell. The solution of quinhydrone reference half-cell must be freshly prepared every day to ensure a steady potential.

c) Silver-silver chloride electrodes: Standard silver electrodes, approximately 5 in. long, were purchased from Beckman Instrument, Inc. The electrodes were cleaned with mild detergent, then with concentrated ammonium hydroxide, and finally with distilled water. The electrodes were made anodes in a cell using a platinum cathode and 1 M hydrochloric acid as electrolyte. The current was regulated with a rheostat to about 5 ma from a 1.5 volts battery so that a small stream of hydrogen was noticed at the platinum electrode. The electrolysis process was continued for four hours. The electrodes during and after electrolysis were protected from direct light.[22]

d) Agar-potassium nitrate bridges: The bridges were pyrex tubes 1 cm. i.d. bent to a U shape. They were filled with a hot cooked mixture of 8 grams U.S.P. agar-agar from Fisher Scientific Co. and 50 grams of chloride-free potassium

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(22). G. J. Janz & H. Taniguchi, Chem. Rev., 53, 397 (1953).

nitrate in 100 ml. of distilled water. When not in use, the bridges were kept in a covered beaker containing saturated solution of potassium nitrate so as to maintain the nitrate concentration and prevent the agar from drying out.

CONSTANT TEMPERATURE CONTROL: A constant temperature water or oil bath was used for the rate measurements. Temperature control was of the order of $\pm$ 0.05°C.

SEALED AMPOULE TECHNIQUE: Since trial experiments showed that the half-life of the reaction studied was of the order of 50 hours at 30°C., the two reactants could be premixed in a volumetric flask; measured volumes of samples were transferred to clean and dry test tubes, cooled and then sealed. The zero time was taken as the time when these tubes were put in the constant temperature bath.

The following is a description of an experiment in detail: Benzyl chloride (0.6370 gr.) was weighed directly into a 50-ml. volumetric flask and diluted to the mark with 0.1 M potassium t-butoxide. Samples, 5 ml. each, were withdrawn, transferred to test tubes, and sealed. The tubes were withdrawn from the bath at certain recorded intervals of time, cooled, opened and their contents transferred quantitatively to a small beaker containing 25 ml. of 1 M sulfuric acid. The chloride content was titrated at once with silver nitrate (Fig. 3).

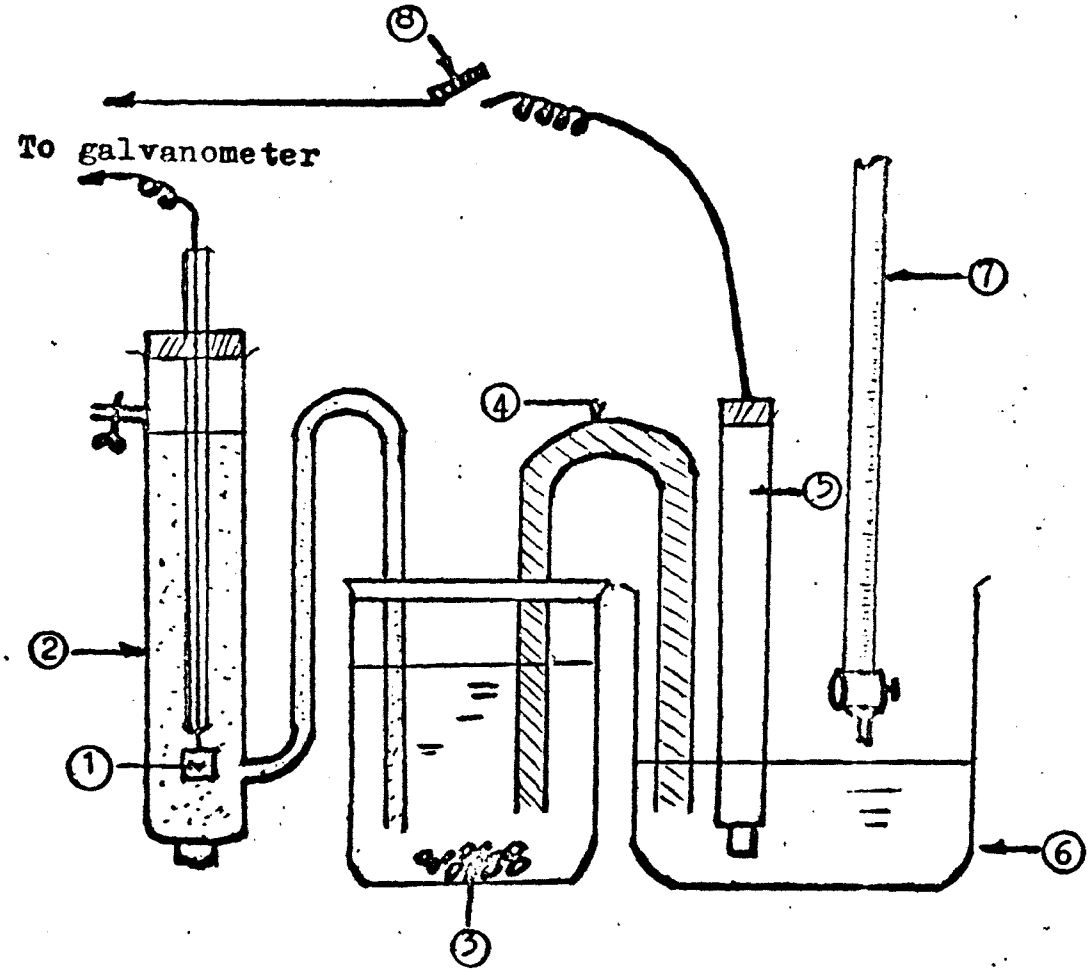

Fig. 3 ELECTROMETRIC METHOD FOR THE DETERMINATION OF CHLORIDE IONS

1. Platinum electrode
2. Quinhydrone half-cell
3. Saturated potassium nitrate solution
4. Agar-potassium nitrate bridge
5. Ag-AgCl electrode
6. Titration vessel
7. Burette
8. Key, single contact

KINETIC DATA

Run 2A

The temperature is 30.0°C.

Concentration of benzyl chloride = 0.03086 mole/liter

Concentration of potassium t-butoxide = 0.29892 mole/liter

Time in hours	19.50	36.80	48.50	67.50
ml. of $AgNO_3$	4.78	8.50	10.80	13.80

Average value of $k = 1.1845 \times 10^{-5}$ liter/mole-sec

Run 2B

The temperature is 30.0°C.

Concentration of benzyl chloride = 0.03349 mole/liter

Concentration of potassium t-butoxide = 0.28982 mole/liter

Time in hours	15.00	26.00	43.00	61.40
ml. of $AgNO_3$	4.60	6.60	10.60	13.70

Average value of $k = 1.0923 \times 10^{-5}$ liter/mole-sec

Run 2C

The temperature is 30.0°C.

Concentration of benzyl chloride = 0.03002 mole/liter

Concentration of potassium t-butoxide = 0.29892 mole/liter

Time in hours	11.80	22.70	34.30	53.80	77.20	102.80
ml. of $AgNO_3$	2.66	5.10	7.10	10.30	13.10	16.20*

Average value of $k = 0.96045 \times 10^{-5}$ liter/mole-sec

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*These points gave rate constants which deviated by more than 15 per cent from the value calculated by least-squares fitting of the data, and were, therefore, excluded from the final calculations.

Run 3A

The temperature is 30.0°C.

Concentration of benzyl chloride = 0.03084 mole/liter

Concentration of potassium t-butoxide = 0.59784 mole/liter

Time in hours	18.75	47.50	66.70	83.80
ml. of $AgNO_3$	7.08	14.50	16.90	19.30

Average value of $k = 0.81646 \times 10^{-5}$ liter/mole-sec

Run 3B

The temperature is 30.0°C.

Concentration of benzyl chloride = 0.03076 mole/liter

Concentration of potassium t-butoxide = 0.59784 mole/liter

Time in hours	14.4	25.50	42.50	60.80
ml. of $AgNO_3$	8.6*	10.00	13.90	17.10

Average value of $k = 0.86517 \times 10^{-5}$ liter/mole-sec

Run 3C

The temperature is 30.0°C.

Concentration of benzyl chloride = 0.03280 mole/liter

Concentration of potassium t-butoxide = 0.59784 mole/liter

Time in hours	11.00	22.00	33.50	53.20	76.50
ml. of $AgNO_3$	7.16*	11.80	14.50*	16.40	21.10

Average value of $k = 0.84751 \times 10^{-5}$ liter/mole-sec

Run 4A

The temperature is 30.0°C.

Concentration of benzyl chloride = 0.06146 mole/liter

Concentration of potassium t-butoxide = 0.59568 mole/liter

Time in hours	18.00	35.30	46.80
ml. of $AgNO_3$	17.80	27.80	32.70

Average value of $k = 1.0600 \times 10^{-5}$ liter/mole-sec

Run 4B

The temperature is 30.0°C.

Concentration of benzyl chloride = 0.06061 mole/liter

Concentration of potassium t-butoxide = 0.59568 mole/liter

Time in hours	13.40	23.50	41.50	60.00
ml. of $AgNO_3$	10.90	18.20	26.10	32.90

Average value of $k = 0.87934 \times 10^{-5}$ liter/mole-sec

Run 4C

The temperature is 30.0°C.

Concentration of benzyl chloride = 0.06001 mole/liter

Concentration of potassium t-butoxide = 0.59568 mole/liter

Time in hours	10.40	21.30	32.80	52.40	75.80
ml. of $AgNO_3$	11.34	18.70	24.30	30.90	36.70

Average value of $k = 0.83993 \times 10^{-5}$ liter/mole-sec

Run 2D

The temperature is 30.4°C.

Concentration of benzyl chloride = 0.03155 mole/liter

Concentration of potassium t-butoxide = 0.29892 mole/liter

Time in hours	18.50	32.00	43.80	54.00	69.00
ml. of $AgNO_3$	7.40	11.30	13.10	14.90	17.30

Average value of $k = 1.4777 \times 10^{-5}$ liter/mole-sec

Run 2E

The temperature is 30.4°C.

Concentration of benzyl chloride = 0.03351 mole/liter

Concentration of potassium t-butoxide = 0.29892 mole/liter

Time in hours	18.30	31.50	43.50	53.50	78.50
ml. of $AgNO_3$	7.40	11.80	14.40	16.00	20.00

Average value of $k = 1.6228 \times 10^{-5}$ liter/mole-sec

Run 3D

The temperature is 30.4°C

Concentration of benzyl chloride = 0.03155 mole/liter

Concentration of potassium t-butoxide = 0.59784 mole/liter

Time in hours	17.50	31.00	42.70	53.00	80.00
ml. of $AgNO_3$	9.50	13.60	16.60	18.50	20.70

Average value of $k = 1.1360 \times 10^{-5}$ liter/mole-sec

Run 3E

The temperature is 30.4°C.

Concentration of benzyl chloride = 0.03136 mole/liter

Concentration of potassium t-butoxide = 0.59784 mole/liter

Time in hours	17.30	30.50	42.50	53.20	70.00
ml. of $AgNO_3$	9.60	14.20	17.70	19.10	21.50

Average value of $k = 1.2463 \times 10^{-5}$ liter/mole-sec

Run 4D

The temperature is 30.4°C.

Concentration of benzyl chloride = 0.06137 mole/liter

Concentration of potassium t-butoxide = 0.59568 mole/liter

Time in hours	14.70	28.00	39.80	51.50	75.00
ml. of $AgNO_3$	14.90	23.70	29.10	32.80	39.80

Average value of $k = 1.0061 \times 10^{-5}$ liter/mole-sec

Run 4E

The temperature is 30.4°C.

Concentration of benzyl chloride = 0.06072 mole/liter

Concentration of potassium t-butoxide = 0.59568 mole/liter

Time in hours	14.40	27.50	39.50	74.50
ml. of $AgNO_3$	14.60	24.10	29.10	43.20*

Average value of $k = 1.0503 \times 10^{-5}$ liter/mole-sec

Run 8A

The temperature is 40.7°C.

Concentration of benzyl chloride = 0.10203 mole/liter

Concentration of potassium t-butoxide = 0.09880 mole/liter

Time in hours	8.30	30.30	41.00	54.50	66.90
ml. of $AgNO_3$	7.40	24.20	29.00	33.60	38.30

Average value of $k = 3.6207 \times 10^{-5}$ liter/mole-sec

Run 8B

The temperature is 40.7°C.

Concentration of benzyl chloride = 0.10198 mole/liter

Concentration of potassium t-butoxide = 0.09880 mole/liter

Time in hours	8.10	17.90	29.50	41.00	54.20
ml. of $AgNO_3$	7.70	14.50	23.30	29.30	33.10

Average value of $k = 3.5829 \times 10^{-5}$ liter/mole-sec

Run 6A

The temperature is 50.3°C.

Concentration of benzyl chloride = 0.10096 mole/liter

Concentration of potassium t-butoxide = 0.09880 mole/liter

Time in hours	8.90	20.40	27.40	33.20	45.50	56.50
ml. of $AgNO_3$	17.30	32.00	37.80	41.70	47.80	50.70*

Average value of $k = 8.7787 \times 10^{-5}$ liter/mole-sec

Run 6B

The temperature is 50.3°C.

Concentration of benzyl chloride = 0.10252 mole/liter

Concentration of potassium t-butoxide = 0.09880 mole/liter

Time in hours	8.20	19.70	27.00	32.60	44.70	55.90
ml. of $AgNO_3$	17.50	32.30	39.90*	44.00*	47.20	53.00

Average value of $k = 8.7674 \times 10^{-5}$ liter/mole-sec

Run 6C

The temperature is 50.3°C.

Concentration of benzyl chloride = 0.10085 mole/liter

Concentration of potassium t-butoxide = 0.09880 mole/liter

Time in hours	8.00	19.50	26.60	32.40	44.50
ml. of $AgNO_3$	17.40	33.10	39.80	43.70	48.90

Average value of $k = 9.5288 \times 10^{-5}$ liter/mole-sec

Run 7A

The temperature is 59.7°C.

Concentration of benzyl chloride = 0.10040 mole/liter

Concentration of potassium t-butoxide = 0.09880 mole/liter

Time in hours	4.60	7.50	15.00	22.00	27.40	31.40	43.00
ml. of $AgNO_3$	18.60	26.50	37.50*	47.70*	52.50	54.30	59.00

Average value of $k = 18.340 \times 10^{-5}$ liter/mole-sec

Run 7B

The temperature is 59.7°C.

Concentration of benzyl chloride = 0.10129 mole/liter

Concentration of potassium t-butoxide = 0.09880 mole/liter

Time in hours	4.5	7.3	15.0	16.3	21.8	27.3	31.3
ml. of $AgNO_3$	16.0*	26.0	39.3	43.2	49.9	53.1	55.0

Average value of $k = 19.206 \times 10^{-5}$ liter/mole-sec

Run 9A

The temperature is 69.8°C.

Concentration of benzyl chloride = 0.10017 mole/liter

Concentration of potassium t-butoxide = 0.09880 mole/liter

Time in hours	4.87	7.25	9.88	11.30	14.25
ml. of $AgNO_3$	33.40	42.80	48.30	51.90	54.40

Average value of $k = 40.685 \times 10^{-5}$ liter/mole-sec

Run 9B

The temperature is 69.8°C.

Concentration of benzyl chloride = 0.10003 mole/liter

Concentration of potassium t-butoxide = 0.09880 mole/liter

Time in hours	4.63	7.00	9.70	11.53	14.02	17.00
ml. of $AgNO_3$	32.60	41.30	49.20	54.00*	55.10	61.20*

Average value of $k = 43.321 \times 10^{-5}$ liter/mole-sec

Calculation of the energy of activation E_a for the reaction between benzyl chloride and potassium t-butoxide in t-butyl alcohol, between 30.4° and 69.8°C.

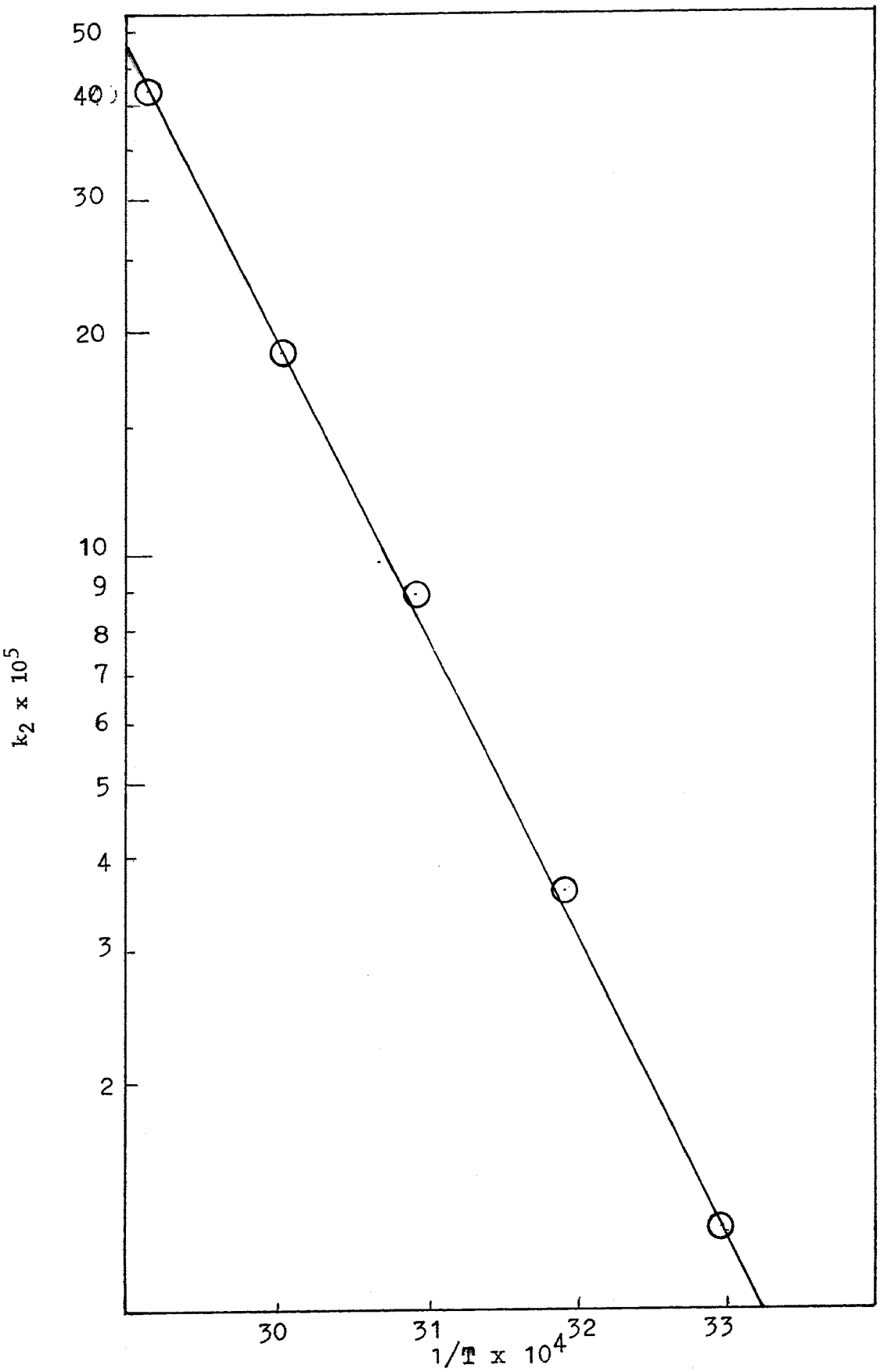
TABLE I DATA FOR ACTIVATION ENERGY CALCULATION

Avg. k, l./mol-sec	t°C.	T, °K	1/T x 10^4
1.2565 x 10^{-5}	30.4	305.56	32.72
3.6018 x 10^{-5}	40.7	313.86	31.86
9.0241 x 10^{-5}	50.3	323.46	30.90
18.7730 x 10^{-5}	59.7	332.86	30.04
42.0030 x 10^{-5}	69.8	342.96	29.16

Figure 4 is a depiction of these results.

E_a = Slope x 2.303 x 1.987 = 18,200 calories.

Fig. 4 PLOT OF SECOND-ORDER RATE CONSTANTS ON A LOG SCALE VS. 1/T FOR DETERMINATION OF ARRHENIUS ACTIVATION ENERGY, E_a.


50
40
30
20
10
9
8
7
6
5
4
3
2
$k_2 \times 10^5$
30
31
32
33
$1/T \times 10^4$

IV. DISCUSSION

THE ORDER OF THE REACTION

The reaction was investigated under pseudo-unimolecular conditions in trial experiments. The presence of a large excess of t-butoxide ion as compared to the initial concentration of the halide in the reaction medium gave rise to first-order kinetics. The data of such experiments fitted the appropriate equation,

$$\ln A/(A-X) = kt$$

Where A is the initial concentration of benzyl chloride, and X the amount decomposed at time t.

Reactions carried out with varying concentrations of benzyl chloride and t-butoxide ion seem to indicate that the over-all reaction order is two, first order in each of the reactants.

The results of Table II suggest the following rate law,

$$\text{Rate} = \frac{dX}{dt} = k_2 \left[\text{Benzyl chloride}\right] \left[\text{t-Butoxide}\right]$$

which is readily integrated to

$$k_2 = \frac{1}{A-B} \ln \frac{B(A-X)}{A(B-X)}$$

Where A = initial concentration of benzyl chloride

B = initial concentration of potassium t-butoxide

X = amount reacting in time t

TABLE II

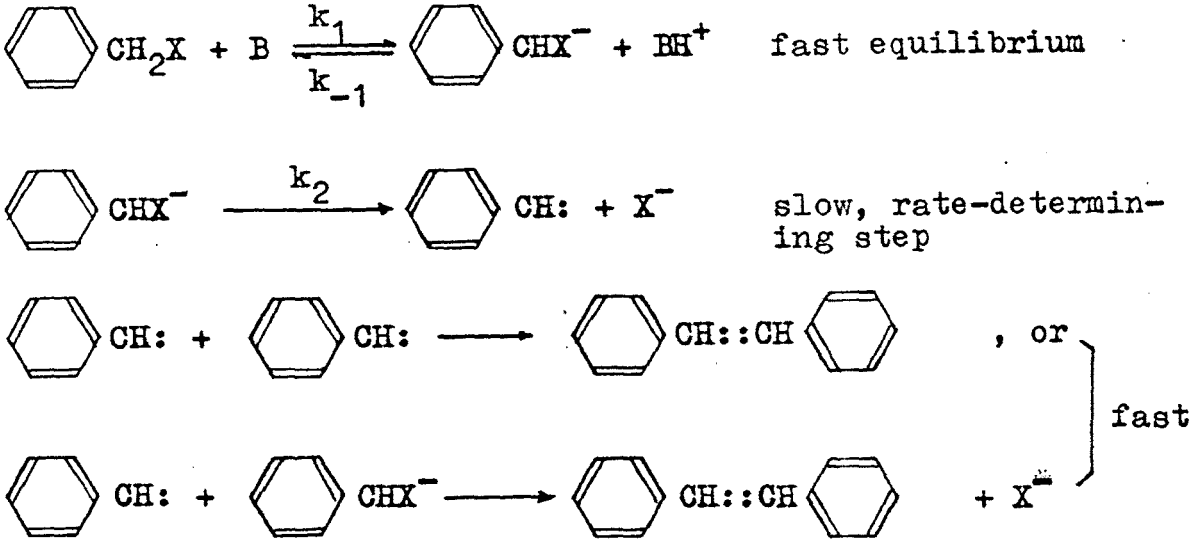
Second Order Rate Constants for Reaction of Benzyl Chloride with Potassium t-Butoxide in t-Butyl Alcohol at 30.0°C.

Run No.	Conc. of Halide	Conc. of t-Butoxide	$k_2 \times 10^5$ M^{-1} Sec
2A	0.03086	0.29892	1.18450
2B	0.03349	0.28982	1.09230
2C	0.03002	0.29892	0.96045
		average	1.01240
3A	0.03084	0.59784	0.81646
3B	0.03076	0.59784	0.86517
3C	0.03280	0.59784	0.84751
		average	0.84301
4A	0.06146	0.59568	1.06000
4B	0.06061	0.59568	0.87934
4C	0.06001	0.59568	0.83993
		average	0.92642

MECHANISMS

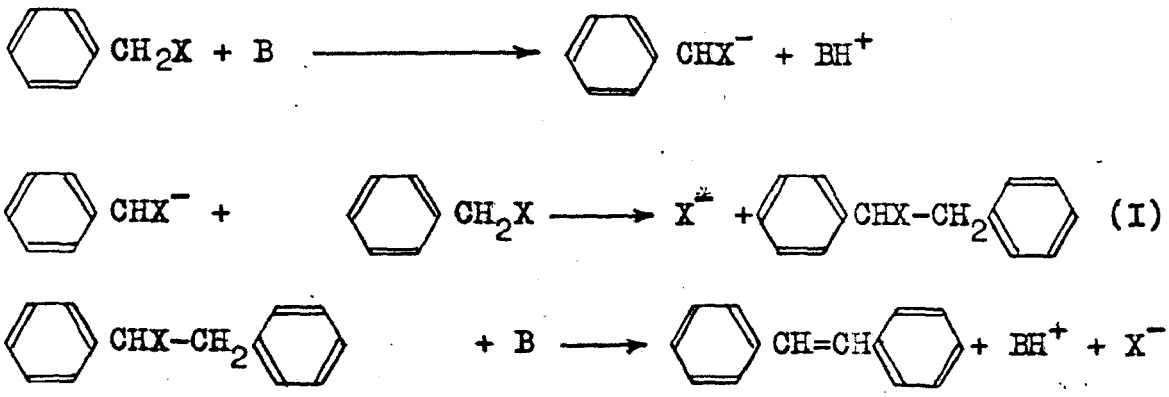
The formation of stilbene from benzyl compounds by the action of strong base can be accounted for by at least two distinct mechanisms.[20]

(A) THE α-ELIMINATION MECHANISM:



The operation of this mechanism in the p-nitrobenzyl series has recently been proved using kinetic methods.[9,10]

(B) THE BIMOLECULAR ALKYLATION-DISPLACEMENT MECHANISM:[8]

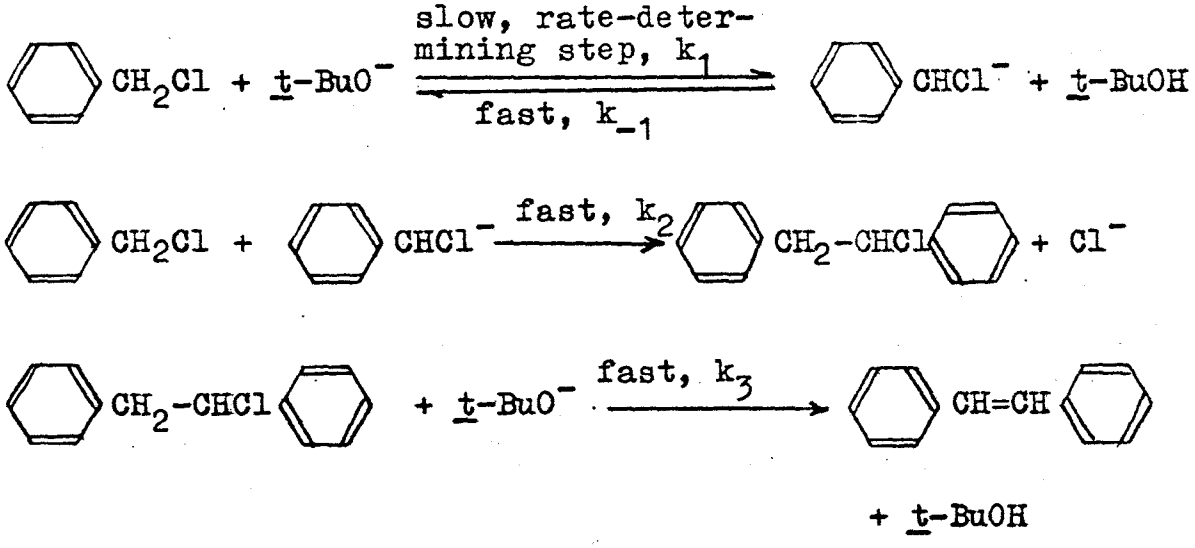


Isolation of the intermediate "dimeric" halide (I) at low temperatures was taken as an evidence for the occurence of this mechanism in the benzyl and the diphenylmethyl series.[17]

Mechanisms (A) and (B) are distinguishable kinetically, provided that the proton transfer in the first step in each mechanism is faster than the succeeding steps. Mechanism (A) would demand first-order kinetics in the benzyl halide, while mechanism (B) is satisfied by second-order kinetics in the organic halide.

At a first glance, our results seem to favor the α-elimination mechanism. However, we have not carried out any deuterium exchange experiments to ascertain whether or not the proton transfer step is a fast equilibrium. We feel, therefore, that an alternative mechanism is possible.

(C)



Mechanisms (A) and (C), but not (B), lead to second-order over-all kinetics as is evidenced from the following:

(A)'

$$\frac{d[X^-]}{dt} = k_2[C_6H_5CHX^-]$$

But

$$[C_6H_5CHX^-] = K_e[C_6H_5CH_2X][B]$$

Where K_e = equilibrium constant = k_1/k_{-1}

Therefore,

$$\frac{-d[X^-]}{dt} = \frac{k_1k_2}{k_{-1}}[C_6H_5CH_2X][B]$$

$$= k'_2[C_6H_5CH_2X][B]$$

Where $k'_2 = k_1k_2/k_{-1}$

(C)'

$$-\frac{d[C_6H_5CH_2Cl]}{dt} = k_1[C_6H_5CH_2Cl][\underline{t}\text{-BuO}^-]$$

Where k_1 is second-order rate constant

We believe that the isolation of the "dimeric" halide by Hauser and co-workers[17] at low temperatures does not necessarily indicate that mechanism (B) is operative in liquid ammonia. Only kinetic measurements coupled with

tracer techniques on the parent compound as well as on this "dimeric halide" would help us in establishing the true mechanism.

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APPENDIX

Least Squares Computer Program

```
C       CALCULATION OF SECOND ORDER RATE CONSTANTS
C       REACTION TYPE B(A)+S(B)=PRODUCTS
        DIMENSION XML(300),M(300),X(300),Y(300),XSLOP(300),DEL(300),T(300)
        READ 106,N
        DO 6 I=1,N
        READ 108,TEMP
        PUNCH 200,TEMP
        READ 106,L
        DO 6 K=1,L
        READ 106,M
        XM=M
        READ 100,(XML(I),I=1,M)
        READ 100,(M(I),I=1,M)
        READ 110,A,B,R,S,CF
        PUNCH 107,A,B
        DO 2 I=1,M
        T(I)=3600.*M(I)
        X(I)=XML(I)*CF/5.
    2   Y(I)=LOGF(B*(A-R*X(I))/(A*(B-S*X(I))))/(A-B)
C       LEAST-SQUARES FITTING OF DATA
        SUMX=0.0
        SUMY=0.0
        SUMXY=0.0
        SUMX2=0.0
        DO 3 I=1,M
        SUMX=T(I)+SUMX
        SUMY=Y(I)+SUMY
        SUMXY=T(I)*Y(I)+SUMXY
    3   SUMX2=T(I)**2+SUMX2
        DEN=XM*SUMX2-SUMX**2
        SLOPE=(XM*SUMXY-SUMX*SUMY)/DEN
        CONST=(SUMX2*SUMY-SUMX*SUMXY)/DEN
        PUNCH 101,SLOPE,CONST
C       CALCULATE OF INDIVIDUAL SLOPES
        DO 4 I=1,M
        CALCK=Y(I)/T(I)
        DEL(I)=SLOPE-CALCK
    4   PUNCH 102,T(I),CALCK,DEL(I)
C       STATISTICAL TREATMENT OF THE DATA
        DEL1=0.0
        DEL2=0.0
        DO 5 I=1,M
        DSLOP=ABSF(DEL(I))
        DEL1=DSLOP+DEL1
    5   DEL2=DSLOP**2+DEL2
        ADEV=DEL1/XM
```

```
      PUNCH 103,ADEV
      STD=SQRTF(DEL2/(XN*(XN-1.)))
      PUNCH 104,STD
      PERCT=200.*STD/SLOPE
    6 PUNCH 105,PERCT
      STOP
  100 FORMAT(12E6.3)
  101 FORMAT(2X,7HSLOPE =,E13.5,14HLITER/MOL -S  C,5X,9HCONSTANT=,E12.5)
  102 FORMAT(2X,5HTIME=,F10.3,2X,10HEXP CONST=,  11.5,2X,4HDEV=,E12.5)
  103 FORMAT(2X,19HAVERAGE DEVIATION =,E13.5)
  104 FORMAT(2X,20HSTANDARD DEVIATION =,E13.5)
  105 FORMAT(2X,42HPERCENT DEVIATION AT 95 C  D  UCE LEVEL =,F7.3)
  106 FORMAT(I6)
  107 FORMAT(1X,13HCONC OF RCL =,F8.5,5X,14H  T OF BUO- =,F8.5)
  108 FORMAT(E6.1)
  110 FORMAT(6E12.6)
  200 FORMAT(15H1TEMPERATURE IS,F6.1,1X,1HC)
      END
```

TEMPERATURE IS 30.0 C

2A CONC OF RCL = .03046 CONC OF DUO- = .29892
SLOPE = 0.11845E-04LITER/MOLE-SEC CONSTANT= -0.13659E-00
TIME= 70200.000 EXP CONST=0.10155E-04 DEV= 0.13870E-05
TIME=132480.000 EXP CONST=0.10625E-04 DEV= 0.12203E-05
TIME=174600.000 EXP CONST=0.11032E-04 DEV= 0.81317E-06
TIME=243000.000 EXP CONST=0.11333E-04 DEV= 0.51154E-06
AVERAGE DEVIATION = 0.10580E-05
STANDARD DEVIATION = 0.66194E-06
PERCENT DEVIATION AT 95 CONFIDENCE LEVEL = 11.177

2B CONC OF RCL = .03349 CONC OF DUO- = .29892
SLOPE = 0.10923E-04LITER/MOLE-SEC CONSTANT= -0.13960E-01
TIME= 54000.000 EXP CONST=0.11557E-04 DEV=-0.63426E-06
TIME= 93600.000 EXP CONST=0.10046E-04 DEV= 0.87665E-06
TIME=154000.000 EXP CONST=0.10894E-04 DEV= 0.29240E-07
TIME=221040.000 EXP CONST=0.10907E-04 DEV= 0.15880E-07
AVERAGE DEVIATION = 0.38901E-06
STANDARD DEVIATION = 0.31250E-06
PERCENT DEVIATION AT 95 CONFIDENCE LEVEL = 5.722

2C CONC OF RCL = .03002 CONC OF DUO- = .29892
SLOPE = 0.96045E-05LITER/MOLE-SEC CONSTANT= -0.82418E-02
TIME= 42480.000 EXP CONST=0.91225E-05 DEV= 0.48162E-06
TIME= 81720.000 EXP CONST=0.96342E-05 DEV=-0.79609E-07
TIME=123480.000 EXP CONST=0.94417E-05 DEV= 0.16288E-06
TIME=193680.000 EXP CONST=0.96733E-05 DEV=-0.68776E-07
TIME=277920.000 EXP CONST=0.95309E-05 DEV= 0.73630E-07
AVERAGE DEVIATION = 0.17330E-06
STANDARD DEVIATION = 0.11725E-06
PERCENT DEVIATION AT 95 CONFIDENCE LEVEL = 2.442

3A CONC OF RCL = .03084 CONC OF DUO- = .59784
SLOPE = 0.81646E-05LITER/MOLE-SEC CONSTANT= 0.17734E-01
TIME= 67500.000 EXP CONST=0.82701E-05 DEV=-0.10548E-06
TIME=171000.000 EXP CONST=0.85710E-05 DEV=-0.40635E-06
TIME=240120.000 EXP CONST=0.79491E-05 DEV= 0.21552E-06
TIME=301680.000 EXP CONST=0.83174E-05 DEV=-0.15274E-06
AVERAGE DEVIATION = 0.22002E-06
STANDARD DEVIATION = 0.14318E-06
PERCENT DEVIATION AT 95 CONFIDENCE LEVEL = 3.507

3B CONC OF RCL = .03076 CONC OF DUO- = .59784
SLOPE = 0.86517E-05LITER/MOLE-SEC CONSTANT= 0.62565E-01
TIME= 91800.000 EXP CONST=0.93890E-05 DEV=-0.73732E-06
TIME=153000.000 EXP CONST=0.89960E-05 DEV=-0.34436E-06
TIME=218880.000 EXP CONST=0.89592E-05 DEV=-0.30758E-06
AVERAGE DEVIATION = 0.46308E-06
STANDARD DEVIATION = 0.35516E-06
PERCENT DEVIATION AT 95 CONFIDENCE LEVEL = 8.210

3C CONC OF RCL = .03280 CONC OF DUO- = .59784
SLOPE = 0.84751E-05LITER/MOLE-SEC CONSTANT= 0.22243E+00

TIME= 79200.000 EXP CONST=0.12479E-04 DEV =-0.40043E-05
TIME=191520.000 EXP CONST=0.84798E-05 DEV =-0.46938E-08
TIME=275400.000 EXP CONST=0.97432E-05 DEV =-0.12682E-05
AVERAGE DEVIATION = 0.17591E-05
STANDARD DEVIATION = 0.17148E-05
PERCENT DEVIATION AT 95 CONFIDENCE LEVEL = 40.466
CONC OF RCL = .06146 CONC OF DUO- = .9568
1A SLOPE = 0.10600E-04LITER/MOLE-SEC CONSTANT= 0.64217E-01
TIME= 64800.000 EXP CONST=0.11616E-04 DEV =-0.10166E-05
TIME=127080.000 EXP CONST=0.11072E-04 DEV =-0.47259E-06
TIME=168480.000 EXP CONST=0.10996E-04 DEV =-0.39598E-06
AVERAGE DEVIATION = 0.62840E-06
STANDARD DEVIATION = 0.48540E-06
PERCENT DEVIATION AT 95 CONFIDENCE LEVEL = 9.159
CONC OF RCL = .06061 CONC OF DUO- = .9568
1B SLOPE = 0.87934E-05LITER/MOLE-SEC CONSTANT= 0.13853E-01
TIME= 48240.000 EXP CONST=0.87872E-05 DEV = 0.61172E-08
TIME= 84600.000 EXP CONST=0.93181E-05 DEV =-0.52476E-06
TIME=149400.000 EXP CONST=0.87213E-05 DEV = 0.72085E-07
TIME=216000.000 EXP CONST=0.88956E-05 DEV =-0.10222E-06
AVERAGE DEVIATION = 0.17630E-06
STANDARD DEVIATION = 0.15574E-06
PERCENT DEVIATION AT 95 CONFIDENCE LEVEL = 3.542
CONC OF RCL = .06001 CONC OF DUO- = .9568
1C SLOPE = 0.83993E-05LITER/MOLE-SEC CONSTANT= 0.16607E-00
TIME= 37440.000 EXP CONST=0.11986E-04 DEV =-0.35864E-05
TIME= 76680.000 EXP CONST=0.10786E-04 DEV =-0.23864E-05
TIME=118080.000 EXP CONST=0.10060E-04 DEV =-0.16602E-05
TIME=160640.000 EXP CONST=0.92501E-05 DEV =-0.85074E-06
TIME=272880.000 EXP CONST=0.89731E-05 DEV =-0.57381E-06
AVERAGE DEVIATION = 0.18115E-05
STANDARD DEVIATION = 0.10575E-05
PERCENT DEVIATION AT 95 CONFIDENCE LEVEL = 25.181

```
TEMPERATURE IS  30.4 C
CONC OF RCL =  .03155      CONC OF BUD- =  .1 9792
2D SLOPE =  0.14777E-04LITER/MOLE-SEC      CONSTANT=  0.19245E+00
   TIME= 66600.000   EXP CONST=0.17344E-04   DEV =-0.25672E-05
   TIME=115200.000   EXP CONST=0.17271E-04   DEV =-0.24943E-05
   TIME=157800.000   EXP CONST=0.15603E-04   DEV =-0.82588E-06
   TIME=194400.000   EXP CONST=0.15472E-04   DEV =-0.69551E-06
   TIME=248400.000   EXP CONST=0.15737E-04   DEV =-0.96012E-06
   AVERAGE DEVIATION =  0.15086E-05
   STANDARD DEVIATION =  0.86312E-06
   PERCENT DEVIATION AT 95 CONFIDENCE LEVEL =  11.682
CONC OF RCL =  .03351      CONC OF BUD- =  .1 9892
2E SLOPE =  0.16228E-04LITER/MOLE-SEC      CONSTANT=  0.35415E-01
   TIME= 65880.000   EXP CONST=0.16326E-04   DEV =-0.97156E-07
   TIME=113400.000   EXP CONST=0.17167E-04   DEV =-0.93863E-06
   TIME=156600.000   EXP CONST=0.16581E-04   DEV =-0.35266E-06
   TIME=192600.000   EXP CONST=0.15936E-04   DEV = 0.29067E-06
   TIME=282600.000   EXP CONST=0.16458E-04   DEV =-0.22997E-06
   AVERAGE DEVIATION =  0.38182E-06
   STANDARD DEVIATION =  0.24002E-06
   PERCENT DEVIATION AT 95 CONFIDENCE LEVEL =  2.958
CONC OF RCL =  .03155      CONC OF BUD- =  .1 9784
3D SLOPE =  0.11360E-04LITER/MOLE-SEC      CONSTANT=  0.17422E-01
   TIME=111600.000   EXP CONST=0.11477E-04   DEV =-0.11663E-06
   TIME=153720.000   EXP CONST=0.11534E-04   DEV =-0.17457E-06
   TIME=190800.000   EXP CONST=0.11425E-04   DEV =-0.65083E-07
   AVERAGE DEVIATION =  0.11876E-06
   STANDARD DEVIATION =  0.09733E-07
   PERCENT DEVIATION AT 95 CONFIDENCE LEVEL =  1.530
CONC OF RCL =  .03136      CONC OF BUD- =  .1 9784
3E SLOPE =  0.12463E-04LITER/MOLE-SEC      CONSTANT=  0.31424E-01
   TIME= 62280.000   EXP CONST=0.12799E-04   DEV =-0.33569E-06
   TIME=109800.000   EXP CONST=0.12579E-04   DEV =-0.11597E-06
   TIME=153000.000   EXP CONST=0.13202E-04   DEV =-0.73812E-06
   TIME=191520.000   EXP CONST=0.12335E-04   DEV = 0.13085E-06
   TIME=252000.000   EXP CONST=0.12605E-04   DEV =-0.14130E-06
   AVERAGE DEVIATION =  0.29239E-06
   STANDARD DEVIATION =  0.18815E-06
   PERCENT DEVIATION AT 95 CONFIDENCE LEVEL =  3.019
CONC OF RCL =  .06137      CONC OF BUD- =  .1 9564
4D SLOPE =  0.10061E-04LITER/MOLE-SEC      CONSTANT=  0.69675E-01
   TIME= 52920.000   EXP CONST=0.11417E-04   DEV =-0.13566E-05
   TIME=100800.000   EXP CONST=0.11007E-04   DEV =-0.94598E-06
   TIME=143280.000   EXP CONST=0.10595E-04   DEV =-0.53403E-06
   TIME=185400.000   EXP CONST=0.10075E-04   DEV =-0.14225E-07
   TIME=270000.000   EXP CONST=0.10439E-04   DEV =-0.37805E-06
   AVERAGE DEVIATION =  0.64577E-06
   STANDARD DEVIATION =  0.39771E-06
```

PERCENT DEVIATION AT 95 CONFIDENCE LEVEL = 7.906

45 CONC OF BCL = .06072 CONC OF CHO- = .50562

SLOPE = 0.10503E-04LITER/MOLE-SEC CONSTANT= 0.72435E-01

TIME= 51840.000 EXP CONST=0.11517E-04 DEV=-0.10132E-05

TIME= 99000.000 EXP CONST=0.11656E-04 DEV=-0.11523E-05

TIME=142200.000 EXP CONST=0.10860E-04 DEV=-0.35654E-06

AVERAGE DEVIATION = 0.84069E-06

STANDARD DEVIATION = 0.64311E-06

PERCENT DEVIATION AT 95 CONFIDENCE LEVEL = 12.246

TEMPERATURE IS 40.7 C

CONC OF RCL = .10203 CONC OF BUO- = .09880

8A SLOPE = 0.36207E-04LITER/MOLE-SEC CONSTANT= 0.36619E-01

TIME= 2988[illegible].000 EXP CONST=0.33174E-04 DEV= 0.30330E-05

TIME=109080.000 EXP CONST=0.38391E-04 DEV=-0.21845E-05

TIME=147600.000 EXP CONST=0.37094E-04 DEV=-0.88686E-06

TIME=196200.000 EXP CONST=0.35421E-04 DEV= 0.78596E-06

TIME=240840.000 EXP CONST=0.36451E-04 DEV=-0.24390E-06

AVERAGE DEVIATION = 0.14268E-05

STANDARD DEVIATION = 0.87849E-06

PERCENT DEVIATION AT 95 CONFIDENCE LEVEL = 4.853

CONC OF RCL = .10198 CONC OF BUO- = .09880

8B SLOPE = 0.36829E-04LITER/MOLE-SEC CONSTANT= 0.13167E-01

TIME= 291[illegible]0.000 EXP CONST=0.35535E-04 DEV= 0.29640E-06

TIME= 644[illegible]0.000 EXP CONST=0.33340E-04 DEV= 0.24891E-05

TIME=106200.000 EXP CONST=0.37403E-04 DEV=-0.15743E-05

TIME=147600.000 EXP CONST=0.37715E-04 DEV=-0.18863E-05

TIME=195170.000 EXP CONST=0.34749E-04 DEV= 0.10801E-05

AVERAGE DEVIATION = 0.14652E-05

STANDARD DEVIATION = 0.82118E-06

PERCENT DEVIATION AT 95 CONFIDENCE LEVEL = 4.584

TEMPERATURE S 50.3 C

CONC OF RCL = .10096 CONC OF BUO- = .09880

4A SLOPE = 0.17787E-04LITER/MOLE-SEC CONSTANT= -0.16520E-01

TIME= 32040.000 EXP CONST=0.84437E-04 DEV= 0.33493E-05

TIME= 73440.000 EXP CONST=0.88445E-04 DEV=-0.65806E-06

TIME= 98640.000 EXP CONST=0.88150E-04 DEV=-0.36370E-06

TIME=119520.000 EXP CONST=0.88156E-04 DEV=-0.36972E-06

TIME=163800.000 EXP CONST=0.87153E-04 DEV= 0.63305E-06

AVERAGE DEVIATION = 0.10748E-05

STANDARD DEVIATION = 0.78487E-06

PERCENT DEVIATION AT 95 CONFIDENCE LEVEL = 1.788

CONC OF RCL = .10252 CONC OF BUO- = .09880

4B SLOPE = 0.76787E-04LITER/MOLE-SEC CONSTANT= 0.78667E-01

TIME= 29520.000 EXP CONST=0.91390E-04 DEV=-0.37430E-05

TIME= 70920.000 EXP CONST=0.91147E-04 DEV=-0.34999E-05

TIME=160920.000 EXP CONST=0.83888E-04 DEV= 0.37587E-05

TIME=201240.000 EXP CONST=0.90434E-04 DEV=-0.27868E-05

AVERAGE DEVIATION = 0.34471E-05

STANDARD DEVIATION = 0.20032E-05

PERCENT DEVIATION AT 95 CONFIDENCE LEVEL = 4.571

CONC OF RCL = .10085 CONC OF BUO- = .09880

4C SLOPE = 0.95288E-04LITER/MOLE-SEC CONSTANT= 0.21227E+00

TIME= 26800.000 EXP CONST=0.94744E-04 DEV= 0.54411E-06

TIME= 70200.000 EXP CONST=0.98033E-04 DEV=-0.27444E-05

TIME= 95760.000 EXP CONST=0.10037E-03 DEV=-0.50835E-05

TIME=116640.000 EXP CONST=0.99869E-04 DEV=-0.45807E-05

TIME=160200.000 EXP CONST=0.94435E-04 DEV= 0.85335E-06

AVERAGE DEVIATION = 0.27612E-05

STANDARD DEVIATION = 0.16641E-05

PERCENT DEVIATION AT 95 CONFIDENCE LEVEL = 3.493

TEMPERATURE IS 59.7 C

CONC OF RCL = .10040 CONC OF BUO- = .09880

7A SLOPE = 0.18340E-03LITER/MOLE-SEC CONSTANT= -0.64070E-01

TIME= 16560.000	EXP CONST=0.18043E-03	DEV= 0.29642E-05
TIME= 27000.000	EXP CONST=0.18048E-03	DEV= 0.29221E-05
TIME= 79200.000	EXP CONST=0.18104E-03	DEV= 0.23589E-05
TIME= 98640.000	EXP CONST=0.18684E-03	DEV=-0.34427E-05
TIME=113040.000	EXP CONST=0.17996E-03	DEV= 0.34405E-05
TIME=154800.000	EXP CONST=0.18327E-03	DEV= 0.13103E-06

AVERAGE DEVIATION = 0.25432E-05

STANDARD DEVIATION = 0.12463E-05

PERCENT DEVIATION AT 95 CONFIDENCE LEVEL = 1.359

CONC OF RCL = .10129 CONC OF BUO- = .09880

7B SLOPE = 0.19206E-03LITER/MOLE-SEC CONSTANT= -0.27920E-00

TIME= 26280.000	EXP CONST=0.17832E-03	DEV= 0.13741E-04
TIME= 54000.000	EXP CONST=0.17256E-03	DEV= 0.19497E-04
TIME= 58680.000	EXP CONST=0.19236E-03	DEV=-0.29795E-06
TIME= 78480.000	EXP CONST=0.20142E-03	DEV=-0.93591E-05
TIME= 98280.000	EXP CONST=0.19048E-03	DEV= 0.15811E-05
TIME=112680.000	EXP CONST=0.18445E-03	DEV= 0.76134E-05

AVERAGE DEVIATION = 0.86815E-05

STANDARD DEVIATION = 0.48890E-05

PERCENT DEVIATION AT 95 CONFIDENCE LEVEL = 5.091

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 TEMPERATURE IS  69.8 C
7A CONC OF RCL =  .10017      CONC OF BUO- =  .09880
   SLOPE =  0.40685E-03LITER/MOLE-SEC      CONSTANT=  0.39645E+0
   TIME= 17532.000   EXP CONST=0.40222E-03   DIV= 0.46277E-05
   TIME= 26100.000   EXP CONST=0.43140E-03   DIV=-0.24549E-04
   TIME= 35568.000   EXP CONST=0.41731E-03   DIV=-0.10464E-04
   TIME= 40680.000   EXP CONST=0.44056E-03   DIV=-0.33712E-04
   TIME= 51300.000   EXP CONST=0.40059E-03   DIV= 0.62547E-05
   AVERAGE DEVIATION =  0.15921E-04
   STANDARD DEVIATION =  0.97703E-05
   PERCENT DEVIATION AT 95 CONFIDENCE LEVEL =  4.803
9B CONC OF RCL =  .10003      CONC OF BUO- =  .09880
   SLOPE =  0.43321E-03LITER/MOLE-SEC      CONSTANT= -0.25094E-0
   TIME= 16668.000   EXP CONST=0.40687E-03   DIV= 0.26338E-04
   TIME= 25200.000   EXP CONST=0.41574E-03   DIV= 0.17475E-04
   TIME= 34920.000   EXP CONST=0.44633E-03   DIV=-0.13115E-04
   TIME= 50832.000   EXP CONST=0.42176E-03   DIV= 0.11457E-04
   AVERAGE DEVIATION =  0.17096E-04
   STANDARD DEVIATION =  0.10418E-04
   PERCENT DEVIATION AT 95 CONFIDENCE LEVEL =  4.809

   STOP END OF PROGRAM AT STATEMENT 0006 + 0. LINES.
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VITA

The author was born on September 27, 1937 to Mr. and Mrs. Sui Tong Chen in Taipei, Taiwan, Republic of China.

He received his primary and secondary education in Taipei. He has received his college education in National Taiwan University, Taipei, Taiwan, China, and received a Bachelor of Science Degree in Chemical Engineering in June, 1960. He came to the United States in September, 1963 and enrolled in the Graduate School of the University of Missouri at Rolla.